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Nanoimprint lithography resist profile inversion for lift-off applications

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TITLE RUNNING HEAD: Lift-off process for nanoimprint lithography

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ABSTRACT: A method is described in which the tapered features that are inherent to nanoimprint lithography are inverted to allow successful lift-off. A mold of the relief is created by in-filling the imprinted resist with hydrogen silsesquioxane (HSQ) before selectively removing the resist with O_2 plasma. Nanoscale etch masks have been created by lift-off from the negative HSQ profile and used to create high-aspect-ratio structures in materials that are hard to plasma etch.

KEYWORDS: Nanoimprint lithography, lift-off, re-entrant, spin-on glass, HSQ.

Lithography generally involves the creation of three dimensional structures from two dimensional patterns or masks. Pattern transfer from a master is then followed by either an additive or subtractive process. The latter involves the removal of material by etching, whereas the former involves the addition of material either by selective deposition or by lift-off.

Nanoimprint lithography uses a physical mould to transfer the relief from a three-dimensional master into a softer, deformable material. As a result the resolution is not limited by the wavelength of the light used as in photolithography, and the patterning speed not limited by the slow electron beam lithography writing time. These features make the technique one of great promise for the mass replication of nanostructures even for features smaller than 10 nm [1, 2]. Applications that demand such resolution include magnetic and optical data storage, polymer electronics, nanofluidic devices and optoelectronics [3]. The alternative techniques for patterning at this resolution, such as EUV and X-Ray lithography have the disadvantage that they are very expensive. In contrast NIL is relatively cheap [4] and tooling has been developed by companies such as EVG, Obducat, Molecular Imprints and Nanonex. The variant of the process, known as Roller-NIL lends itself to roll-to-roll processing giving even greater scope of reducing the cost [5, 6]. It also provides superior filling of the relief of the imprint master with only low imprint force [7].

NIL involves the local displacement of a resist layer by a master mold which is subsequently released. The master is then re-used for as long as it remains undamaged. As a result, this puts constraints on the properties of the master; it should be designed firstly to allow high quality imprints to be made and secondly to have a long lifetime, i.e. to create a large number of imprints, since its creation is often very expensive. The latter can be influenced by the choice of resist, the anti-adhesion properties and the shape of the relief of the master. The resist is typically a polymer that can be cross-linked by heat, ultraviolet light or a combination of both. This allows its displacement to occur at lower pressure whilst the resist has low viscosity. The polymer is then cross-linked before the master is released. The release is made easier by engineering the properties of the resist or applying an anti-adhesion layer to the master. Finally and significantly, the master relief has a slight positive profile to prevent the resist being trapped and pulled off during release.

For many applications the imprinted pattern subsequently needs to be transferred into a different material. Typically this is a subtractive process achieved by etching. For this, the residual layer needs to be removed by dry etching. Since this process enlarges the imprinted features, the residual layer is typically designed to be as small as possible and can be ~10-20 nm for UV-cured polymers. The need to limit the residual layer thickness means the surface roughness of the target substrate has to be less than a few nanometers for accurate pattern transfer, restricting the range of materials for which NIL can be reliable. Since the resist is then used as a mask material during a subsequent etching process, success depends on the polymer's etch resistance. As a result NIL typically gives features with aspect ratios up to ~4 [4]. Creation of high aspect ratio features requires amplification techniques such as the use of an intermediate hard mask.

Instead of the subtractive process described above, nanoimprint lithography can be used with additive processes such as lift-off. At its most basic, this involves removal of the residual layer, vacuum deposition of another material followed by the removal of the imprinted resist along with any material deposited on top. However, there are several requirements to make this work well in practice. Firstly the resist should be easily removable from the substrate and secondly there should be a negative, or re-entrant, resist profile. The standard way of achieving these is to use a bi-layer resist stack [8-10]. The top layer is known as the imaging layer, and the lower layer is the lift-off layer. After descumming, the lower layer is eroded more than the upper layer to create a negative lift-off profile. The challenge for this technique is to have sufficient control of the undercut in order not to affect other nanoscale features in close proximity.

This paper describes an alternative to this process that takes advantage of the inherent positive profile that is required in NIL. As described above, an optimised master has a slightly tapered profile to allow easy release. This is shown schematically in Fig. 1a. Future improvements to master creation might involve steepening the side walls in order to improve this control, but the fundamental need for an ever so slightly tapered profile will not be changed unless shrinkable resists are tolerated or there is perfect anti-adhesion. In general, UV-curing polymers suffer less shrinkage during polymerization than thermally cured resists, therefore less change in the critical dimensions [4].

This process involves the deposition of a second material that in-fills the relief in the imprinted resist and planarises the surface. The material is chosen to have a complementary etch chemistry to the imprinted resist. In this work a spin-on-glass such as HSQ (hydrogen silsesquioxane) was used. HSQ has the advantage that there is no organic component, is poorly etched in O_2 plasma and has the ability for excellent planarization [11]. After a simple etch back step (Figure 2b), the imprint resist is selectively removed by dry etching in O2 plasma to leave a cast of the master relief with a negative lift-off profile (Figure 2c). The use of highly dissimilar materials for the 1st and 2nd layers allows the first layer to be selectively removed without affecting the 2nd layer.

Figure 3 shows an example of using this new lift-off process for the creation of a nanoporous Ni film intended for subsequent use as a hard etch mask. The negative resist profile can just be observed prior to metal deposition in Figure 3a and after evaporating a 50nm-thick Ni layer gives rise to the shadowed region observable in Figure 3b. This shadowed region is the characteristic of a structure that produces successful lift-off.

The thickness of material that can be successfully patterned by this lift-off technique depends on the depth of the imprinted resist and the thickness of the residual layer. In fact, more material can potentially be deposited if the residual layer is thicker, although there will be a limit imposed by the anisotropy of the O_2 plasma etching process. In contrast, the thickness of material that can be successfully patterned by the conventional lift-off technique depends on the thickness of the under-layer. Figure 4a shows a metal dot array that has been created with this process. The nanoimprinted pattern consisted of a hexagonal array of 220 nm pillars of resist on a 600 nm pitch. In practice, we have found that much thicker layers can be deposited as a result of the shrinkage of the resist aperture during deposition as shown schematically in Figure 4c. This leads to a sloping sidewall of the deposited material. In the extreme case, using a circular aperture, a cone of deposited material can be created as shown in Figure 4b. The thickness of material deposited then depends on the size of the initial resist aperture and the rate at which the aperture closes up with deposition. The thicknesses of metal deposited were nominally 150nm and 425nm in Figs 4a and 4b respectively.

A further advantage of this process is its insensitivity to the residual layer thickness (Figure 5). In standard NIL, the residual layer must be removed across the whole sample. If the sample is rough, then there will be large variations in the residual layer thickness, which will directly or indirectly lead to non-uniformity in the pattern transfer. A lift-off layer in the traditional lift-off process will reduce this sensitivity by planarising the surface. However the variation of thickness will affect the control of the undercut, which can be an issue in closely-spaced nanostructures. It is worth re-iterating that the undercut in the process described here derives from the profile of imprinted nanostructure, i.e. it is molded rather than controllably removed as in conventional lift-off. Such molded lift-off profiles provide greater precision and tolerance in the process. In the process described here, the uniformity of the residual layer in the imprinted resist film is of lesser importance. The accuracy of the pattern transfer now depends on firstly the ability of the HSQ to planarise the top surface and secondly the uniformity of the upper level or peaks in the imprinted resist film. By and large, the latter depends on the quality of the imprint stamp and its infilling during the imprint step, factors more readily controlled in NIL than the uniformity of the residual layer thickness.

There are other subtle differences in the two lift-off processes which may or may not be advantageous. For the standard etching and bi-layer lift-off process, the critical dimension in the patterned layer is determined by the bottom of the imprinted structure, corresponding to the top of the protrusions of the master. The reverse is the case for our process. This makes the generation of the master mold and how it was created a significant factor in the accuracy of pattern transfer.

Another aspect of the lift-off process is the ability to release the underlying resist with the unwanted material on top from the substrate. Nanoimprint resists are usually cross-linked polymers that are resistant to many conventional solvents and other wet etches. However, the spin-on-glasses can be etched, for example by HF-based solutions. Therefore, one option for lift off is to use an HF-based etch followed by a plasma descum to remove the residual imprint resist underneath the spin-on-glass. Alternatively there are release layers that can be bought commercially which are soluble in conventional solvents. These can be very thin layers, e.g. 10 nm, and can successfully release nanoimprint resists to allow lift-off as well as the reworking of conventional nanoimprint lithography. The restriction is that the release layer should not intermix with the imprint resist and thus could restrict the choice of solvents used. The use of a release layer can reduce the damage caused by acid etches to allow successful pattern transfer to sensitive samples.

In order to demonstrate that the process works for fine features, a 120nm pitch grating master was tested. Figure 6b shows the result after the lift-off of 70nm-thick Ni on a silicon substrate. The pattern also included larger grating features that also simultaneously lifted off successfully (Fig 6a).

In order to demonstrate the usefulness of this technology, the thick metal masks have been used as an etch mask during the dry etching of gallium nitride nanorods. Figure 7 shows an SEM image of an array of nanorods, where the length was only limited by the thickness of the GaN starting material. A broken nanorod is shown lying on top of the others to highlight the high aspect ratio that has been achieved through the use of a Ni etch mask in Cl_2/Ar plasma. As a result, the process has opened up a new field within the area of semiconductor nanophotonics. Notably the fabricated GaN nanorods array showed superb wafer-scale uniformity and the process has already been successfully demonstrated on 4-inch wafers. Examples of further applications include the nanoscale structuring of other hard-to-etch materials such as sapphire within light-emitting diodes, and discrete track recording for next generation data storage.

To conclude, we have demonstrated a robust lift-off process for nanoimprint lithography. The process opens up a range of opportunities by combining the resolution that can be achieved by NIL with the properties of materials that are otherwise hard to pattern through subtractive processes. As an example we have created high-aspect-ratio gallium nitride nanorods with this technique.

EXPERIMENTAL DETAILS

A commercial nanoimprint system (Obducat Sindre 400 system) was used to create patterns on either a silicon wafer or a GaN/sapphire template. For the fine features shown in Figure 6, the initial thickness of the imprint resist was 40 nm, which gave a residual layer of 10-20 nm and a structure depth of 30-40 nm as measured by AFM. For the coarser features that have been presented, the structure depth was ~ 200-300 nm. Onto the top of all imprints, a layer of HSQ (FOx-12, Dow Corning) was spun that would give a nominal planar thickness of ~100 nm. This layer was etched back to the level of the imprint by CHF_3 plasma in an Plasmalab 80 RIE dry etch system (Oxford Instruments Plasma Technology). This was directly followed by O_2 plasma to remove the exposed imprint resist. Ni was deposited on the samples by electron beam evaporation (Edwards EB3) and then the unwanted material was lifted off in buffered oxide etch for a few seconds. A scanning electron microscope (Hitachi S-4300) was then used to characterize the results.

The GaN nanorods were created using a ~200nm-thick Ni nanodot array as a mask during Cl_2/Ar plasma etching in a Plasmalab System 100 (Oxford Instruments Plasma Technology). Details of the etch conditions will be published separately.

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FIGURE CAPTIONS

Figure 1. a) Positive resist profile resulting from successful imprinting b) Negative profile necessary for successful lift-off.

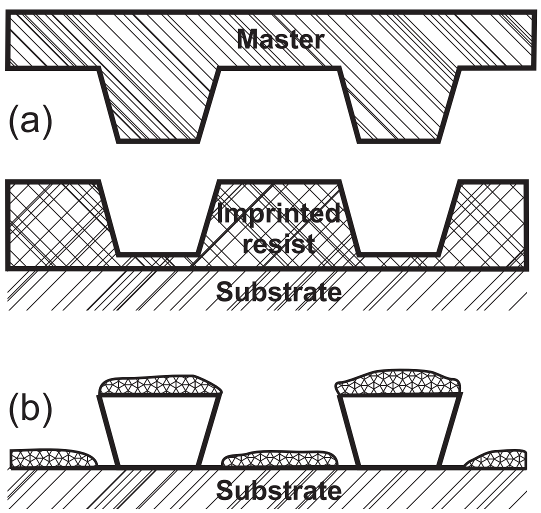

Figure 2. a) Use of further layer, such as spin-on-glass, to infill imprint, b) Etch-back of spin-on-glass residual layer, and c) removal of imprint resist.

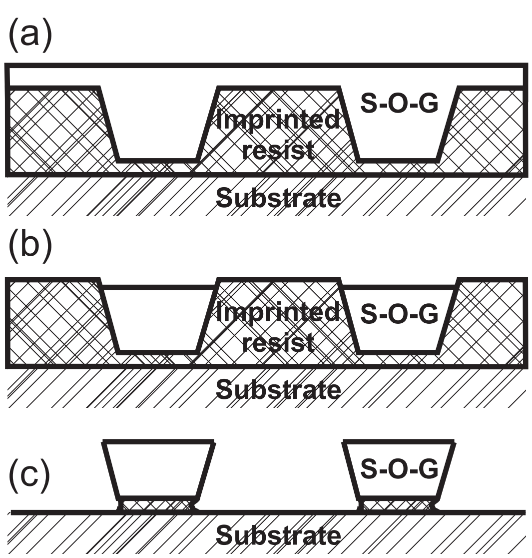

Figure 3. SEM images from the creation of a nanoporous Ni film using the new process. a) HSQ mold of the imprint master, b) after vacuum deposition of 50nm Ni, c) after lift-off revealing the nanoporous Ni film.

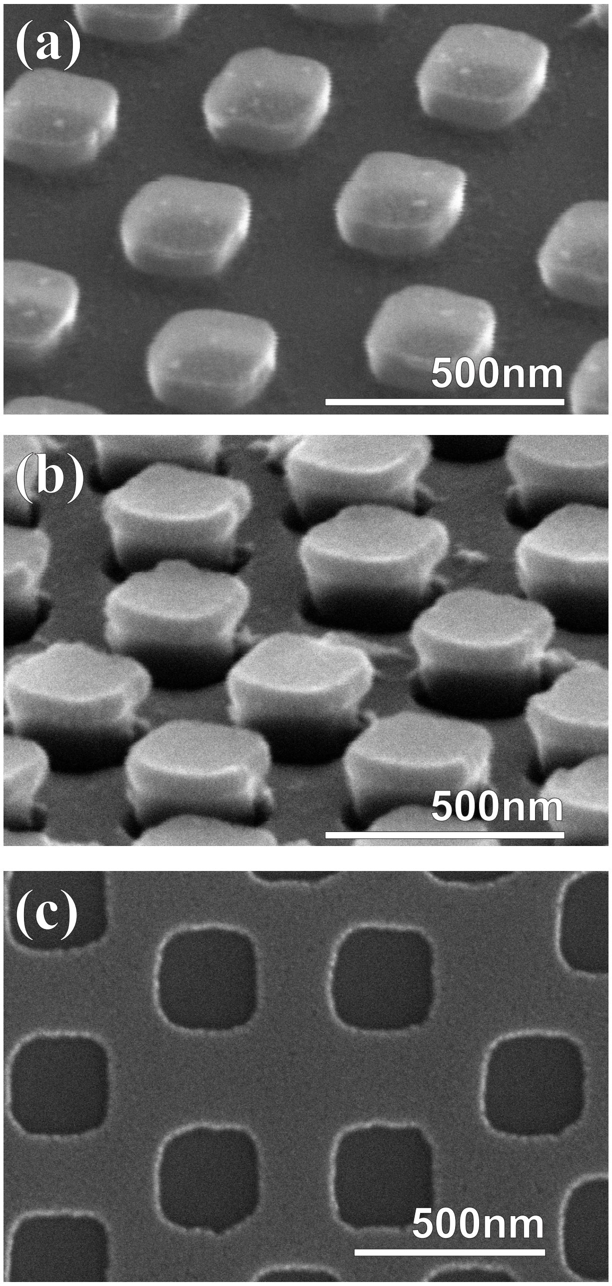
(a)
500nm
(b)
500nm
(c)
500nm

Figure 4. Metal dot array created via lift-off. The nominal amount of metal deposited was a) 150nm, and b) 425nm. c) Schematic showing the creation of tapered nanostructures with a height that exceeds the thickness of the imprinted resist.

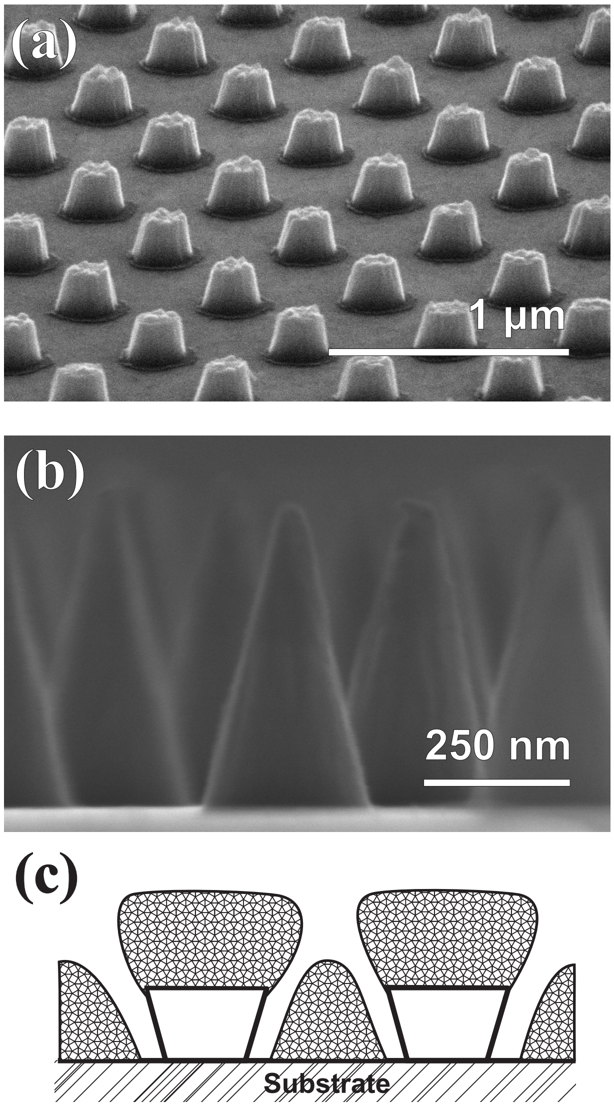

Figure 5. a) Conventional nanoimprint on rough surface, b) New process on rough surface, followed by c) creation of lift-off profile on rough surface.

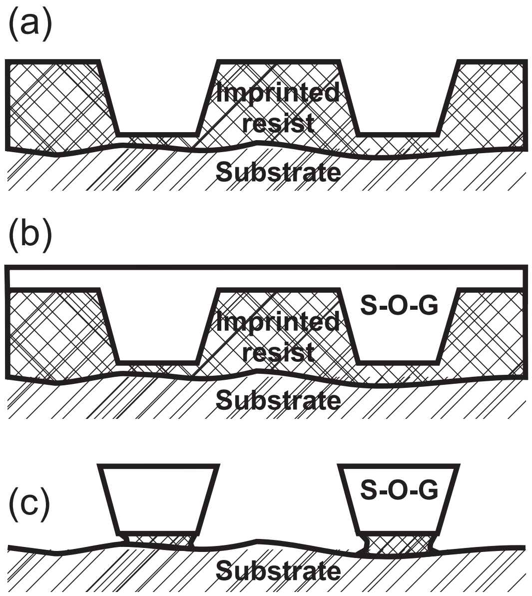

Figure 6. SEM images showing the verification of the process with a 70 nm Ni layer on a silicon substrate. The imprint master consists of a range of features with different size and density. Large scale strips are imaged in (a) and narrow stripes with a pitch of 120 nm are imaged in (b).

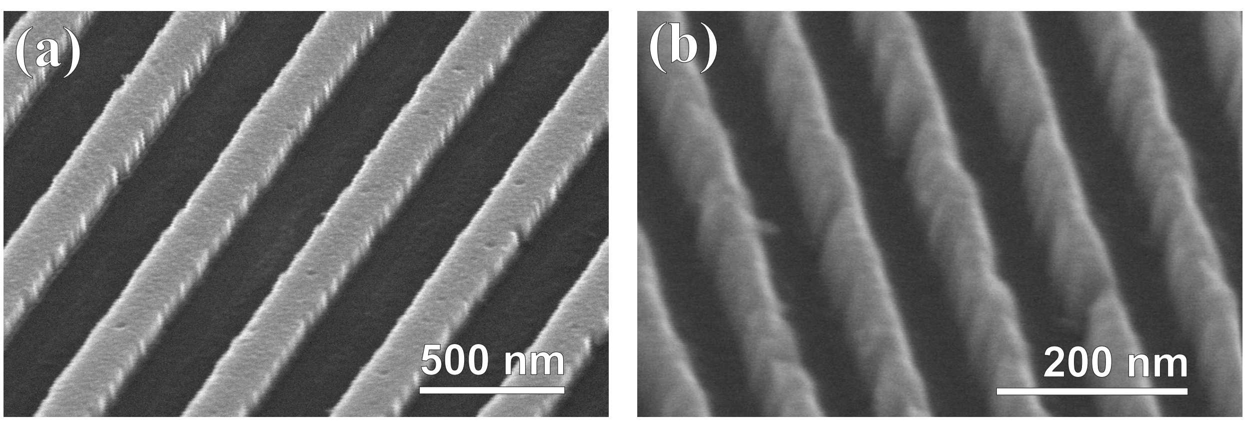

Figure 7. SEM image of a gallium nitride nanorod array, on top of which is resting a single broken nanorod that is 4.2 microns long and ~200nm in diameter.